NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 2422

STUDY OF CHROMIUM-FRIT-TYPE COATINGS FOR HIGH-TEMPERATURE

PROTECTION OF MOLYBDENUM

By D. G. Moore, L. H. Bolz, J. W. Pitts
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National Bureau of Standards

NACA

Washington

July 1951

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

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SUMMARY

The achievement of more compact and efficient power plants for aircraft is dependent, among other factors, on the perfection of heat-resisting materials that are superior to those in current use.

Molybdenum is one of the high-melting metals (melting point, 4750° F). It is fairly abundant and also can be worked into many of the shapes required in modern power plants. To permit its widespread use at elevated temperatures, however, some means must first be found to prevent its rapid oxidation. The application of a protective coating is one method that might be used to achieve this goal.

In the present work, a number of chromium-frit-type coatings were studied. These were bonded to molybdenum specimens by firing in controlled atmospheres to temperatures in the range 2400° to 2700° F. The durability of the coatings was then studied, principally by means of oxidation tests under load in the range of 1500° to 1800° F and by flame tests in the range of 2000° to 3000° F. The results may be summarized as follows:

1. Frit (glass), when used in conjunction with the chromium in the coating, gave coatings with considerably better durability than similar coatings containing no frit.

2. Optimum protection at 2800° F was obtained when the frit was diffused into the previously fired frit-free chromium coating structure through application of a seal coat.

3. The resistance of the chromium-frit-type coatings to cracking by thermal strain, or by rapid creep, was not particularly good but, because of excellent adherence and the tendency of the glassy phase to reseal the fissures, cracking of the coating did not cause rapid failure but rather a weakening in the coating structure from which failure might begin.

4. At 2800° F and with no loading, the most durable coating protected the molybdenum for a maximum of $7\frac{1}{2}$ hours.

5. The maximum temperature at which the chromium-frit-type coatings remained intact without flow in a high-velocity gas stream from an oxyacetylene torch was approximately 3000° F.

6. Maximum life achieved from coated specimens under load in an air atmosphere was 917 hours at 1500° F (0.6-percent creep), 2210 hours at 1650° F (1.7-percent creep), and 3275 hours at 1800° F (1.2-percent creep). At any one test temperature higher creep rates resulted in shorter life.

INTRODUCTION

One of the properties of molybdenum metal which restrict its use in jet-engine applications is its poor resistance to oxidation. Above its melting point of 1463° F, the molybdenum trioxide evaporates rapidly, giving no protection to the metal.

A number of attempts have been made to protect molybdenum against this rapid oxidation by the application of a suitable coating. An earlier study in this laboratory (reference 1) resulted in several coating compositions which gave short-time (less than 1 hr) protection in high-velocity gas streams of 3000° to 3500° F. Other laboratories have also worked on the problem, but there are no published reports describing these studies.

Recent work with titanium-carbide ceramal demonstrated that both excellent adherence and good high-temperature protection against oxidation could be achieved when chromium-frit[1] coatings were applied to this material (reference 2). The fact that chromium forms a solid solution with molybdenum at elevated temperatures (reference 3) indicated that similar coatings, when properly applied and fired, might be effective in protecting molybdenum. The high thermal expansion of chromium as compared with that of molybdenum was expected to be an undesirable feature, inasmuch as the coating would be in tension rather than in compression after firing and cooling; however, it was believed possible that the glass present in the coating would tend to flow sufficiently under operating conditions to seal any cracks that might occur, and thus provide protection. A few exploratory applications showed that the chromium-frit coatings could be bonded to

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[1]The word frit, as used in this paper, refers to the glasslike ingredient of the coating.

molybdenum by relatively simple laboratory procedures and that the resulting coatings, while showing some tendency to craze, were nevertheless promising in their effectiveness in protecting the metal from oxidation at elevated temperatures. Because of these results, a more complete investigation of chromium-frit coatings was undertaken.

The present report, which gives the results of this investigation, is based upon research carried out at the National Bureau of Standards under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

The authors wish to express their appreciation to Mr. Howard E. Swanson of the Constitution and Microstructure Section of the National Bureau of Standards for contributing the data on the X-ray diffraction analysis of the diffusion layer, and to Miss Mary A. Mason of the Enameled Metals Section of the National Bureau of Standards for obtaining the thermal expansion data.

MATERIALS

The molybdenum used for preparing specimens was of commercial purity and was made by the powder metallurgy process. A spectrochemical analysis showed tungsten, silicon, and manganese to be present in minor amounts (0.01 to 1 percent). Trace constituents (less than 0.01 percent) were calcium, copper, iron, and magnesium.

Electrolytic chromium powder was used in the preparation of the coatings. The spectrochemical analysis and the particle size range of the powder are given in table 1.

The compositions of the frits used in the study are listed in table 2.

PREPARATION AND APPLICATION OF COATINGS

Compositions

The compositions of all chromium-bearing coatings (base coats) referred to in this report are given in table 3, while table 4 lists the compositions of the seal, or glaze coats. These seal coats, which were applied over many of the previously fired chromium-type coatings, were fired at a temperature about 200° F lower than the base-coat firing temperature. When the coatings are identified by two numbers, the first number identifies the base coat and the second number identifies

the seal coat. Thus, M-37-13 refers to a base coat of M-37 with a seal coat of M-13 applied over the M-37.

The frit used in all of the chromium-frit base coats was an alkali-free composition, with the assigned number 331. It was selected because previous tests had indicated that its ingredients were noncorrosive toward the more common heat-resisting alloys at temperatures above 1500° F (reference 4). The 331 frit was one of a series of 100 non-corrosive frits which had been prepared. It was selected from this group on the basis of freedom from excessive attack on the crucible during smelting, suitable thermal expansion, and appropriate fusion characteristics.

Seal coat M-13 was described in an earlier study of molybdenum coatings (reference 1), while M-43, having a lower viscosity, was prepared especially for this study.

Methods of Preparing and Applying Coating Slips

In all coatings except M-41, the coating slip consisted of a water suspension of the coating ingredients floated with a 5-percent admixture of a commerical grade of Florida kaolin. The M-41 slip consisted of a mixture of chromium powder and Ethyl Cellosolve with no clay or water added.

When preparing the water-suspension slips, the ingredients as listed in table 3 were placed in a 1-gallon porcelain jar mill with 1-inch-diameter porcelain balls and milled for 3 hours. This treatment gave a suspension of creamlike consistency which is commonly known as a "slip."

All coatings were applied by dipping. This involves immersing the previously sandblasted molybdenum specimen into the slip and then removing the piece and allowing it to drain. By adjusting the water content and by addition of the proper electrolytes, the thickness of coating after draining could be controlled within narrow limits.

Firing Treatment

After drying at about 200° F, the coatings were bonded to the molybdenum by heating to elevated temperatures in a controlled atmosphere. High-frequency induction furnaces were constructed for this work. Two furnace types were used. Figures 1 and 2 are schematic drawings of these two furnaces.

For the firing operation, the specimens were suspended by molybdenum wires in such a position as to be surrounded by the susceptor. The susceptor was heated by induction and the heat was passed from the susceptor to the specimens by radiation and convection. Temperature control was manual. A calibrated optical pyrometer sighted on the specimens was used for temperature measurement. With this manual control and a 25-kilowatt mercury-arc converter as the power source, the temperature could be maintained within ±30° F. The time of firing, unless otherwise stated, was 5 minutes at temperature for each firing.

Atmospheres

Three types of furnace atmospheres were employed during the firing tests, purified hydrogen, tank argon, and partial vacuum. The oxygen was removed from the hydrogen by first passing the gas through a palladium catalyst and then through activated alumina to remove the water. No attempt was made to purify the argon. The partial vacuum was maintained at a pressure of 10 millimeters of mercury, which was the best attainable with the particular equipment used.

LABORATORY TEST PROCEDURES AND RESULTS

Prolonged Oxidation Tests in Air in Range of 1500° to 1800° F

Specimens of 0.080-inch-diameter molybdenum wire, 9 inches long, were chosen for the oxidation tests in air in the range of 1500° to 1800° F. The specimens were straightened by cold-work at room temperature and after sandblasting were coated with the M-39-13 combination. The scope of this study necessitated that only one coating be subjected to these prolonged testing periods. For this purpose the M-39-13 coating was selected as being typical of the class of coatings under study, and as having good possibilities, under conditions involving creep, because of its glass content (approximately 30 percent by volume in the M-39 base coat).

Four furnaces of the type shown in figure 3 were used. Each of these furnaces was explored for temperature distribution by use of a molybdenum specimen with the bead of a platinum to platinum-rhodium thermocouple (made of 30 gage wire) embedded at a point about $4\frac{1}{2}$ inches from one end. In embedding the thermocouple, the specimen was first coated with M-39-13 and then drilled halfway through at its midpoint to form a hole of 0.030-inch diameter. This hole was lined with a chromized layer by packing it with a chromium and alumina mixture and heating the specimen for 1/2 hour at 2700° F in hydrogen. After

removal of the packing material, the thermocouple bead was peened into
the chromized hole and a thin layer of seal coat M-13 was then applied
over the entire specimen to impart additional oxidation resistance.

During calibration, this specimen with an embedded thermocouple
was inserted into the furnace and the temperature distribution deter-
mined, with various settings of the controller, by positioning the center
of the specimen at different vertical locations within the hot zone.
In subsequent tests the specimen was positioned in the furnace so that
the temperature at the middle of the gage length was never more than
10° F higher than that reported. The temperatures at both ends of the
gage length were never more than 15° F lower than the reported value.

Oxidation tests with coated specimens under no load.- At each
of the three test temperatures (1500°, 1650°, and 1800° F), duplicate
specimens were tested with no load beyond the small amount (200 psi)
necessary both to hold the wire in a vertical position and to actuate
the mechanism for recording failure. When failure occurred, the lower
half of the specimen dropped out of the furnace and the weight, falling
on a small switch, short-circuited the thermocouple connected to the
recorder. Thus, the point where the recorder curve suddenly dropped
to a low value gave the time of failure for the specimen.

Table 5 includes the data from the tests made under a no-load
condition.

Oxidation tests with coated specimens under load.- If molybdenum
or any high-molybdenum alloy were to be selected for practical appli-
cation in the temperature range of 1500° to 1800° F, it would quite
likely be operated under conditions of heavy loading. This high stress
operation would cause creep in the metal and for the coating to be
protective it should withstand such creep without cracking. Hence,
the ability of the chromium-frit-type coating M-39-13 to protect the
metal under varying load conditions at the three test temperatures
was studied.

The procedures for this study were the same as those used in the
tests with no load except that provisions were included for measuring
the elongation. The method selected for determining the elongation
or creep of the specimen within the gage length during test may be
briefly outlined as follows.

Platinum wires of 0.010-inch diameter were first twisted tightly
around the coated specimens, 1/2 inch apart, near their midpoint. Seal
coat M-13 was then applied over the wires and the specimens were fired
in argon for 5 minutes at 2550° F. This firing served to cement the

platinum wires firmly in position. Before test, the M-13 seal coat
was ground from the platinum wires at one spot on each wire, the two
spots being alined in a plane parallel to the longitudinal axis. The
platinum at these spots was then polished flat and small scratches
were formed on the polished surfaces for reference points. An initial
measurement of the gage length between the two reference points was
next made by means of a microscope with a stage micrometer. The
precision of this measurement was ±0.01 millimeter or about one part
in 1200.

After making the initial measurement the specimen was inserted in
the furnace and loaded to give the desired stress. After a predetermined
test period the load was released, the specimen was removed from the
furnace, and after cooling to room temperature, the distance between
the gage points was measured in order to compute the percentage
elongation.

Figure 4, which shows the percentage elongation plotted against
time for three specimens tested at 1650° F, is typical of the results
obtained using this procedure. From the standpoint of the present
report, however, the shapes of such curves are of minor interest and
the curves are shown only to illustrate the results obtained by the
test method. The significant feature of the test as it relates to the
coating is the life of the specimen under the various conditions of
temperature, stress, and elongation. Table 5 gives data of this type
for the M-39-13 coating.

Flame Tests in Range of 2000° to 2800° F

The durability of the various coatings in the high-temperature
range was studied by heating the specimens in an oxygen-gas flame. The
equipment used for this purpose is illustrated in figure 5.

In making a test, the specimen was mounted as shown in the photo-
graph and the burner was adjusted so that the temperature of a 1/4-inch
test area, as measured with the optical pyrometer, could be maintained
at any desired value. The specimens were first tested at 2000° F for
1 hour. If no visible signs of failure (as indicated by white fumes
of molybdenum trioxide) were noted, the temperature was increased in
200° F steps up to 2800° F, the specimens being maintained at each
temperature either until failure of the coating occurred or until the
specimen had been subjected to that temperature condition for a period
of 1 hour.

An oxidizing flame was used for all tests. The temperature of the
specimen surface was controlled manually to ±30° F. No emissivity

corrections were made, because spectral emissivity values for the
various coatings were not available. For this reason, the surface
temperatures as listed may be too low by a small amount.

During test, the 1/4-inch-diameter test area at the center of the
specimen was 350° to 500° F higher than the edges of the specimen. A
few optical measurements made on the back of the specimen, directly
behind the test area, indicated a thermal gradient from front to back
of as much as 400° F at the 2800° F test temperature.

Table 6 shows the results of the flame tests with coatings M-37,
M-38, M-39, M-40, and M-41 protected with seal coat M-13 and fired
under various conditions. Table 7 gives the results of a second series
of tests made to determine the effect of the seal coat on coating
durability.

In addition to the above, a few specimens of coatings M-37 and
M-37-13 were flame-tested with the temperature of the specimen surface
increased in 100° F steps and with the testing starting at 2800° F. At
each temperature the testing was continued for 1 minute. Using this
test procedure with a low-velocity oxygen-gas flame, protection of the
molybdenum was good up to a reading of 3400° F. When an oxyacetylene
flame was used, however, giving a blast of high-velocity gases which
directly impinged on the specimen surface, failure of the coating
occurred by flowing of what appeared to be molten chromium at a tempera-
ture as low as 3000° F.

Thermal Shock Tests

Thermal shock tests were made on coated 0.080-inch molybdenum
wire specimens. In one test, the specimens were attached to the outer
periphery of a 3-inch-diameter brass disk which in turn was fixed to
a power-driven shaft turning at 1 rpm. During operation each specimen
passed through the flame of an oxygen-gas torch once a minute. The
flame was adjusted so as to raise the temperature of the specimen
surface to 2000° F in 3 seconds. After passing through the flame, the
surface cooled to below red heat in 2 seconds.

After 60 cycles of this treatment, the specimens appeared about
the same as before the test. At a magnification of about 30 diameters,
however, it could be seen that all the specimens were covered with
numerous surface cracks. Examination of cross sections under the metallo-
graphic microscope revealed that the cracks caused by this type of
thermal shock were confined to the surface and did not extend through
to the diffusion layer. All coatings acted similarly in this test and
no differentiation was possible.

Another thermal shock test that was used was to insert a M-39-13 coated wire specimen at room temperature into the elongation-test furnace (see fig. 3) which was controlled at 1800° F. After soaking for 2 minutes, it was removed and allowed to cool in air. After 25 cycles of this treatment the specimen was sectioned and examined for the presence of cracks in the coating layer. Figure 6 is a photomicrograph of such a section.

Thermal Expansion

Thermal expansion determinations were made with the M-37 and M-39 coating materials over the range of 20° to 700° C using the automatic recording interferograph (reference 5). In each case determinations were made for two specimens and in each case satisfactory agreement was obtained.

Figure 7 shows the expansion curves for the M-37 and the M-39 coating materials. Curves for the reported expansion of chromium (reference 6) and molybdenum (reference 7) are included in the same figure for comparison.

Microstructure

A large number of molybdenum specimens to which the chromium-frit-type coatings had been applied were sectioned and examined with the metallographic microscope. In each case, the presence of a diffusion layer was noted at the interface between the coating and the molybdenum. This layer is well-illustrated in figure 8. It will be seen that the chromium particles in the coating are mechanically anchored to the diffusion layer. It is also evident that the frit or glass phase is held in the network formed by the adhesion of the chromium particles to each other. The thickness of the diffusion layer is affected by the firing temperature, the time of firing, and the coating composition. Figure 9 illustrates how the thickness of the layer varies with time of firing at 2700° F for coating M-39.

Figure 6(b) was taken with polarized light to show the presence of the seal coat which in this case was M-13. The cracks in the diffusion layer occurred when the specimen underwent thermal shock prior to sectioning. Cavities in the coating, similar to that shown in figure 6, were very rare in the various sections examined. The light color of the cavity in figure 6(b) is believed to be caused by the strained condition of the plastic which penetrated the cavity during mounting of the section.

Figure 10 shows the oxidation pockets in the molybdenum that sometimes form under the coating when the coated specimens are subjected to prolonged heating under load.

The structure of the diffusion layer was examined by X-ray diffraction. Sections were prepared by mounting the coated specimens with the surface of the coating at a very small angle to the face of the mount and then grinding and polishing so as to expose a relatively wide band of the diffusion layer. Two specimens, ground at somewhat different angles, were studied.

The sections were placed in a Geiger counter spectrometer using an X-ray beam 1 millimeter by 4 millimeters. Copper radiation was used with a power input of 40 kilovolts and 15 milliamperes. Under the conditions used, the (110) reflections of the chromium and the molybdenum were the only ones sharp enough to measure.

The results of the study using these (110) reflections indicated that the diffusion layer consisted of a solid solution of chromium and molybdenum with a gradation from high chromium at the coating side of the layer to high molybdenum at the side next to the molybdenum. For the specimen on which the prepared surface was nearly parallel to the surface of the diffusion layer, the incident beam could be confined to (a) an area in the diffusion layer adjacent to the molybdenum, (b) an area in the diffusion layer adjacent to the chromium, or (c) intermediate areas. Fairly sharp peaks at a series of values between 2.221 and 2.040 A as well as several quite broad peaks between these limits were obtained at various positions on the section. Because of some curvature of the specimen, the width of the diffusion layer varied considerably from one location to another.

The second specimen, ground at a different angle, showed a much narrower band of diffusion layer which was not as wide as the incident beam. Figure 11 shows a portion of the diffraction pattern obtained when the beam was positioned so as simultaneously to include the coating, the diffusion layer, and the base metal on this second section. The existence of a substantial departure from the base line between the two peaks for chromium and molybdenum, coupled with the absence of any well-defined peaks between these limits, indicates that the layer consists of a continuous solid solution series.

COMPARATIVE SERVICE TESTS WITH COATED MOLYBDENUM

Laboratory tests indicated that the chromium-frit coatings were superior to the all-ceramic coating types described in reference 1,

but some sort of service testing was desirable to substantiate the laboratory data. Fortunately, the Wright Aeronautical Corporation of Wood-Ridge, New Jersey, had the necessary equipment for such tests and at the same time required coated molybdenum parts for instrumentation. This organization therefore kindly consented to cooperate with the Bureau of Standards by comparing several of the coatings under simulated service conditions.

The part selected for testing was a molybdenum protection tube which was 4 inches long with a 3/8-inch outside diameter. This part was used to support an iridium to iridium-rhodium thermocouple in a combustion chamber. The thermocouple, which was exposed to the hot gases, was used to indicate the temperature during test. At an indicated temperature of 2900° to 3000° F the calculated gas velocity was 1560 feet per second, the Mach number was 0.55, the pressure in the test section was 14 inches of mercury (gage), and the fuel-air ratio was 0.040 to 0.041 (highly oxidizing).

The following coatings were included in the tests:

M-13: This all-ceramic coating with high glass content was applied 0.003 to 0.005 inch thick and fired at 2100° F in carbon dioxide (see reference 1).

M-13-35: A first coat (0.003 in. thick) of M-13, a second coat (0.006 to 0.008 in. thick) of M-35 (largely calcined kaolin), and a final seal coat of M-13 were applied. The first coat was fired at 2100° F and the two subsequent coats at 1850° F; all three were fired in carbon dioxide (see reference 1).

M-38-13: A first coat (0.008 in. thick) of M-38 (see table 3) was applied and fired in argon at 2600° F; then a seal coat (0.002 in. thick) of M-13 was applied (see table 4) and fired at the same temperature.

The data from these tests may be summarized as follows:

Tube	Coating	Testing time (min)		Total time for failure (min)
		Below 2900° F	2900° to 3000° F	
1	M-13	2	3	5
2	M-13-35	5	3	8
3	M-38-13	90	10	[a]100
4	M-38-13	48	20	[b]68
5	M-38-13	0	92	[c]92

[a]Coating damaged early in test when it was blown out of duct because of mounting failure.

[b]During initial heating, mounting failed causing tube to scrape against duct. Failure started at this scraped area.

[c]Coating withstood thermal shock resulting from three separate starts.

Figure 12 shows tubes 1 and 4 after failure. The highly oxidizing nature of the combustion gases is evident from the rapid burning and disappearance of the molybdenum throughout about half the circumference of the tube coated with M-13. One of the tubes coated with M-38-13 lasted over 30 times as long at 2900° to 3000° F as the ones coated with the all-ceramic compositions M-13 and M-13-35, indicating a considerable superiority for the chromium-frit coatings. It should be noted, however, that the M-35 layer of the M-13-35 coating was applied considerably thinner than for the specimens reported in reference 1. This change would be expected to increase thermal shock resistance but may have diminished the endurance of the coating.

EXPERIMENTS IN IMPROVING COATING DURABILITY

The results of the flame tests, as shown in table 7, suggested that the glass phase was an important factor in prolonging the life of the chromium-type coatings. In those coatings containing no glass phase (M-37 and M-41) more failures occurred than when the coatings were given the added protection of an M-13 seal coat[2]. Also, it was found

[2]When the M-13 was applied to the M-37 and M-41 base coats, practically all of the M-13 penetrated into the base-coat structure. This did not occur in the case of those base coats which already contained appreciable amounts of glass (frit).

that the M-37 coating when applied without a seal coat gave a much
shorter average life when tested at 1650° F under a load of 15,000 psi
than did M-39-13 which differs from the M-37 only in glass content. The
following failure times were obtained in this comparison:

Specimen	Time for failure (hr)	
	M-37	M-39-13
1	6	83
2	4	20
3	$4\frac{1}{2}$	178

Because of the seeming importance of the glass phase it was felt
that the coatings might be substantially improved by selecting, for the
seal or glaze coat, a composition having a lower fusion temperature
than the M-13. The lower fusion temperature should allow the glass to
flow more readily and thus to seal more effectively any breaks in the
base coat that might occur during test operation.

To test this hypothesis, several new coating combinations were
prepared and tested. Table 8 gives the results of the heating tests in
air under load for these new coatings in comparison with M-39-13. In
order to avoid excessive testing time, a load of 18,500 psi at 1650° F
was selected. As was the case with the earlier data (see table 5) con-
siderable scatter was encountered, and it was necessary to treat the
data statistically. On the basis of this analysis, only one of the
combinations (M-37-13-43) was superior to the M-39-13, based on con-
fidence limits of 95 percent.

In the flame tests made earlier, the M-37-13 coating showed out-
standing durability. Hence, the M-37-13 was compared with the new
M-37-13-43 coating at 2400°, 2600°, and 2800° F. Table 9, which gives
the results of these tests, shows that the two coatings have about equal
durability at 2400° and 2600° F. At 2800° F, however, the M-37-13-43
has an average life of five times that of M-37-13.

DISCUSSION OF RESULTS

In an earlier report (reference 1) several ceramic coatings were
described which successfully protected molybdenum from oxidation in a
high-velocity 3500° F gas stream for periods of from 10 to 45 minutes

under conditions giving a maximum of 2650° F for the metal. That the chromium-frit-type coatings, as herein described, have considerably better durability, at least under conditions existing in the ram jet, is indicated in figure 12. Failure of the ceramic coatings as developed earlier was associated with blistering, whereas the chromium coatings gave no trouble in this respect.

The method of application of the chromium-frit-type coatings was similar to that used for the all-ceramic coatings except that they required a higher firing temperature and a different furnace atmosphere. Table 6 shows that the most durable chromium-frit coatings, from the standpoint of the flame test results, were those that had been fired at 2400° F or higher, in a furnace of the type shown in figure 2, using either tank argon or purified hydrogen as the atmosphere. Because hydrogen was more easily procured than argon and also because it was more easily purified with the laboratory equipment available, hydrogen was used as the standard furnace atmosphere for all subsequent coating applications.

The flame tests, as made with the equipment shown in figure 5, gave a rapid indication of the relative protectiveness of the various coatings. Precautions were taken to achieve good edge coverage but in spite of these precautions, many failures occurred at the edges rather than in the central test area. Therefore, edges and corners having small radii of curvature must be considered as points of weakness with the present coatings. For maximum life, the molybdenum part should be so designed that no radii less than 1/8 inch are included.

The elongation tests show that the chromium-frit-type coating has the ability to creep with the molybdenum if the creep rates are moderate. Figure 4 and table 5 show that in general the time for coating failure at any one temperature decreases with increasing load (i.e., increasing creep rate). However, there are exceptions to this trend in that the specimens with no load, in several cases, show a shorter life than the specimens loaded so as to give a moderate creep rate. There are also large differences in coating life for specimens tested under the same load at a single temperature. The cause of these apparent discrepancies may be associated with occasional flaws in the coating layer of a type shown in the photomicrographs in figure 6. Some protection is afforded at these flaws but they could conceivably be points of weakness from which premature failure could occur.

Figure 8 shows the diffusion layer that forms between the molybdenum and the chromium coating. That the thickness of this layer varies with time of firing is indicated by figure 9, while figure 11 indicates that the layer consists of a solid solution with a continuously varying ratio of chromium to molybdenum.

Figure 7 shows that the thermal expansion of the chromium-frit coatings are substantially higher than the thermal expansion of the molybdenum. Thus, when the coated specimen cools after firing the coating will be placed under tension. If the coating lacks sufficient ductility or strength, a crack pattern would be expected to appear similar to the craze pattern observed on pottery or china when the glaze is of higher expansion than the body. Numerous sections that were examined microscopically showed that widespread crazing did not occur on the first cooling after the firing treatment but that crazing or cracking could be made to occur from severe thermal shock. Figure 6, for example, shows the cracking that resulted from 25 cycles of inserting a coated specimen into a furnace at 1800° F and then quenching in air at room temperature. The finding that similar cracks did not occur during the rotating-wheel thermal shock test at 2000° F was believed caused by the difference in the type of heating and cooling. In the rotating-wheel test, the heating was probably largely confined to the coating surface, whereas in the furnace thermal shock test, the specimens became heated to a uniform temperature throughout.

It should be emphasized that cracking of the coating layer, whether from creep or thermal strain, does not, of itself, constitute failure of the coating. Figure 6(b) shows that the glassy phase tends to flow and reseal the cracks. On the other hand, figure 10 indicates that the cracks are definitely points of weakness. The oxidation pockets, as shown in figure 10(b), obviously have formed underneath cracks in the coating layer. The rate at which these pockets penetrate into the molybdenum, however, must be quite slow inasmuch as a few thermal shock cracks were undoubtedly present near the start of the test and yet the specimen lasted for 178 hours at 1650° F under a loading of 15,000 psi. That the mechanism by which the cracks are sealed is dependent on the glassy phase is evident from the finding that specimens protected with a glass-free coating (M-37), and tested under the same conditions, failed in 4 to 6 hours. Also, the occasional long life of the M-39-13 specimens as reported in table 5 would hardly be possible except for resealing of cracks by the glass present in the coating. From other observations it seems obvious that even the specimen showing the maximum failure time of 3275 hours (at 7500 psi and 1800° F) must have contained numerous thermal cracks in the coating layer that were present from almost the beginning of the test. The thermal cracks should have originated from numerous withdrawals from the furnace necessary for the measurement of specimen elongation.

Figure 8 shows the reason for the excellent adherence of the chromium-frit coatings. When properly applied, some of the chromium present in the coating migrates into the molybdenum to form a diffusion layer. The remaining chromium particles tend to become welded to this diffusion layer and also to each other. The glass, although not plainly evident from figure 8, is enmeshed in the resulting chromium network.

Tables 6, 7, and 8 indicate that the most durable coating results from a first application of a glass-free coating (M-37 or M-41) followed by introduction of the glass in the form of a seal coat. Microscopical examination of sections shows that the glass is absorbed into the somewhat porous base-coat structure during the firing of the seal coat. This, in effect, creates a chromium-glass-type coating after the second firing. Coating M-37-13, which is of this type, was outstanding in flame tests, while a similar coating with the addition of a second seal coat of lower fusibility than the M-13 (i.e., M-43) was, from the indications of the data obtained, the most durable coating tested. The designation of this latter coating is M-37-13-43.

Considering the study as a whole, it is obvious that some of the coatings as currently developed show possibilities for applications at elevated temperatures where long-time protection is nonessential, or at low temperatures (1500° to 1800° F) where the loading is such that the creep rates will be moderate. For a further increase in durability under load in the low-temperature range, the study points to the need for better ductility of the metallic phase of the coating and also to the necessity for improved flow properties of the glass phase. For longer life at the higher temperatures, greater refractoriness of the metallic phase and lower thermal expansion seem to be desirable goals. That lower thermal expansion might be achieved by proper selection and apportionment of the ceramic admixture is indicated by figure 7, in which M-39 (containing 20 parts frit 331) exhibits an appreciably lower thermal expansion than either chromium or M-37 (containing zero parts frit 331).

CONCLUSIONS

The following conclusions are believed justified from the study of chromium-type coatings for the protection of molybdenum:

1. Frit (glass), when used in conjunction with the chromium in the coating, gave coatings with considerably better durability than similar coatings containing no glass.

2. Optimum protection at 2800° F was obtained when the glass was diffused into the previously fired glass-free chromium coating structure through application of a seal coat.

3. The resistance of the chromium-type coatings to cracking by thermal strain, or by rapid creep, was not particularly good but, because of excellent adherence and the tendency of the glassy phase to reseal the fissures, cracking of the coating did not cause rapid failure but rather a weakening in the coating structure from which failure might begin.

4. At 2800° F and with no loading, the most durable coating protected the molybdenum for a maximum of $7\frac{1}{2}$ hours.

5. The maximum temperature at which the chromium-frit coatings remained intact without flow in a high-velocity gas stream from an oxyacetylene torch was approximately 3000° F.

6. Maximum life achieved from coated specimens under load in an air atmosphere was 917 hours at 1500° F (0.6-percent creep), 2210 hours at 1650° F (1.7-percent creep), and 3275 hours at 1800° F (1.2-percent creep). At any one test temperature, higher creep rates resulted in shorter coating life.

7. The chromium-frit-type coatings as described in this report show possibilities for practical use where long-time protection is nonessential at elevated temperatures (2000° to 3000° F metal temperature), or where the loading is such that creep rates will be moderate at temperatures in the range of 1500° to 1800° F.

National Bureau of Standards
    Washington, D. C., July 17, 1950

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    Attack of Various Compounds on Four Heat-Resisting Alloys.
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TABLE 1.- SPECTROCHEMICAL ANALYSIS AND PARTICLE SIZE RANGE

OF MINUS 200 MESH ELECTROLYTIC CHROMIUM POWDER

(a) Spectrochemical analysis.[1]

Relative amounts of elements reported			
Trace (<0.01 percent)	Very weak (<0.01 percent)	Weak (0.01 to 1 percent)	Very strong (>1 percent)
Ag Al Cu Mg Ni Pb Sn Ti	Ca Co Mn Mo	Fe Si	Cr

(b) Particle size range by microprojection[2]

Particle	Size (microns)
Largest	100
Smallest	1
Apparent average	8-10

[1]Analysis by the Spectrochemistry Section of NBS.
[2]Analysis by the Fineness Laboratory of NBS.

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TABLE 2.- BATCH AND OXIDE COMPOSITIONS OF TWO FRITS USED

IN PREPARATION OF COATINGS

(a) Batch compositions.

Ingredient	Parts by weight in -	
	Frit 331	Frit 402C
Potash feldspar	------	4.2
Flint (SiO_2)	38.00	71.9
Hydrated alumina	------	7.8
Borax	------	26.2
Boric acid	11.50	-----
Soda niter ($NaNO_3$)	------	5.5
Whiting ($CaCO_3$)	7.14	1.6
Barium carbonate	56.63	2.8
Zinc oxide	5.00	-----
Beryllium oxide	2.50	-----
	120.77	120.0

(b) Oxide compositions.

Oxide	Percent by weight in -	
	Frit 331 (1)	Frit 402C (2)
SiO_2	38.0	73.3
B_2O_3	6.5	9.1
Al_2O_3	-----	6.6
ZnO	5.0	----
CaO	4.0	.8
BaO	44.0	2.1
BeO	2.5	----
Na_2O	-----	6.7
K_2O	-----	.7
	100.0	99.3

[1]Computed composition.
[2]By chemical analysis.

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TABLE 3.- BATCH COMPOSITIONS FOR FIVE

CHROMIUM-FRIT-TYPE BASE COATS

[Milling time, 3 hr for 1575-gram charge of dry ingredients
in a 1-gal ball mill containing 4000 grams of 1-in.-diam.
porcelain balls unless specified otherwise]

Coating	Coating constituents (parts by weight)					
	Cr powder (a)	Frit 331 (b)	Clay (c)	Water	NaNO$_2$ (d)	Cello-solve
M-37	100	--	5	50	0.04	--
M-38	90	10	5	52.5	.04	--
M-39	80	20	5	52.5	.04	--
M-40	70	30	5	52.5	.04	--
eM-41	100	--	--	----	----	35

[a]Electrolytic grade, minus 200 mesh powder.
[b]See table 2 for composition of frit 331.
[c]Florida kaolin.
[d]Added to give suitable consistency to slip.
[e]Mixed in beaker using manual stirring.

TABLE 4.- BATCH COMPOSITIONS FOR TWO CERAMIC SEAL COATS

[Milling time, 4 hr for 1050-gram charge of dry
 ingredients in 1-gal ball mill containing 4000 grams
 of 1-in.-diam. porcelain balls]

Ingredient	Parts by weight in -	
	M-13	M-43
[a]Frit 402C	80	----
[a]Frit 331	----	100
[b]Fused zirconium oxide (ZrO_2)	20	----
Florida kaolin	5	5
Sodium nitrate[c]	.1	.1
Water	42.5	42.5

[a]See table 2 for frit compositions.
[b]Partially stabilized, sized to pass through No. 40 U. S. Standard
Sieve but to be retained on No. 80 U. S. Standard Sieve.
[c]Added to give suitable consistency to slip.

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TABLE 5.- LIFE OF MOLYBDENUM SPECIMENS COATED WITH M-39-13

WHEN TESTED UNDER LOAD AT 1500°, 1650°, AND 1800° F

Temperature (°F)	Time for failure (hr) at stress of -				
	No load (a)	7500 psi (b)	10,000 psi (b)	15,000 psi (b)	20,000 psi (b)
1500	166 ---	------- -------	917(0.6) --------	71(1.1) 96(1.7)	9 (3.3) -------
1650	382 191 ---	------- ------- -------	284(0.6) 2210(1.7) ---------	83(3.1) 20(1.4) 178(3.3)	3 (4.9) 2 (4.5) -------
1800	4335	3275(1.2)	1059(4.5)	12(3.0)	-------

^{a}Small load of 200 psi was used in order to hold specimen in position
and also to actuate measuring mechanism that recorded failure time.
^{b}Number in parentheses in percentage of total creep as measured
at last determination prior to failure.

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TABLE 6.- RESULTS OF FLAME TESTS OF CHROMIUM-FRIT-TYPE COATINGS, AS

APPLIED TO 1.50- BY 0.75- BY 0.040-INCH MOLYBDENUM SPECIMENS IN

AN INDUCTION FURNACE WITH INDICATED ATMOSPHERES AND SUSCEPTORS

Coating (a)	Cr in base coat (percent by weight)	Firing temperature (°F) (b)	Test temperature (°F) at which failure occurred[c] when fired in -			
			Graphite susceptor		Molybdenum susceptor	
			Vacuum	Argon	Argon	Hydrogen
M-41-13	100	2400	(d)	2600	(d)	2800
		2600	(d)	2000	(e)	(e)
		2700	(d)	(e)	2800	(e)
M-37-13	95	2400	2000	2800	(e)	2800
		2600	2600[f]	2000	(e)	(e)[f]
		2700	(d)	2800[f]	2400[f]	2800[f]
M-38-13	86	2400	2000	2400[f]	2800[f]	(e)
		2600	2400[f]	2600	2800[f]	2800
		2700	2600[f]	2800	2800[f]	2800[f]
M-39-13	76	2400	2400[f]	2600[f]	2400	2800
		2600	2400[f]	2600	2600[f]	2400[f]
		2700	2000	2600[f]	2600[f]	2800[f]
M-40-13	67	2400	(e)	2600	2800	(e)
		2600	2400[f]	2800	2600	2800
		2700	2000[f]	2800	2600[f]	(e)

[a]M-13 seal coat was applied over each base coat to thickness of between 0.002 and 0.003 in. Seal coat was fired for 5 min under same conditions as base coat except at a temperature of about 200° F lower.

[b]Each base coat applied in two applications with 5 min at firing temperature for each coat.

[c]Temperature held constant for 1 hr at 2000° F and then raised in 200° F steps, with 1-hr heating at each intermediate temperature, until either failure of the coating occurred or until 1-hr heating at 2800° F was completed.

[d]Coating damaged during firing.

[e]No failure after 1-hr heating at 2800° F.

[f]Failure at edge which operated approximately 200° F cooler than 1/4-in.-diam. test area.

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TABLE 7.- RESULTS OF FLAME TESTS AT 2600° AND 2800° F WITH

CHROMIUM-TYPE COATINGS BOTH WITH AND WITHOUT SEAL COAT

Coating (1)	Cr in base coat (percent by weight)	Specimens tested	Number of specimens failed after 1-hr heating[2]		
			At 2600° F	At 2800° F	Total
M-41	100	4	2	2	4
M-37	95	4	0	4	4
M-38	86	4	0	4	4
M-39	76	4	0	4	4
M-40	67	4	0	4	4
M-41-13	100	4	0	2	2
M-37-13	95	4	0	1	1
M-38-13	86	4	1	2	3
M-39-13	76	4	0	4	4
M-40-13	67	4	0	4	4

[1]Number 13 following coating identification indicates that seal coat M-13 was applied over the chromium-type base coat. Base coats were fired at 2600° F in dry hydrogen using a molybdenum susceptor while seal coats were fired under same conditions except at 2400° F.
[2]Visible oxidation of molybdenum at any point on specimen was considered coating failure. Each specimen was tested first at 2600° F and if no failure occurred in 1-hr test period, specimen was retested at 2800° F. If failure occurred at 2600° F, no test was made at 2800° F.

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TABLE 8.- COMPARISON OF FAILURE TIMES FOR COATING M-39-13 AND

THREE MODIFIED COATINGS WHEN APPLIED TO 0.080-INCH DIAMETER

MOLYBDENUM WIRES AND TESTED AT 1650° F AND 18,500 PSI

Coating (a)	Failure time (hr) (b)
M-39-13	9 10 3
M-37-43	4 6 $7\frac{1}{2}$
M-37-13	$6\frac{1}{2}$ 9 $12\frac{1}{2}$
M-37-13-43	$16\frac{1}{2}$ 9 $12\frac{1}{2}$
None	1[c]

[a]In each case, first number disignates base coat while succeeding numbers identify seal coats. For example, M-37-13-43 refers to base coat of M-37 with two seal coats, one of M-13 and one of M-43, each applied with separate firings.

[b]Average creep rate at 1650° F with 18,500 psi loading was approximately 0.8 percent per hr. Time for rupture of specimen was taken as failure time.

[c]Failure time of 1 hr is undoubtedly high because of plugging of furnace tube at cold ends by tight packing of molybdenum-trioxide crystals. Tube ends were unplugged every 5 min during test, but molybdenum trioxide quickly reformed. No plugging of furnace tube was noted with any of coated specimens.   NACA

TABLE 9.- COMPARISON OF FAILURE TIMES IN FLAME TEST OF COATINGS

M-37-13 AND M-37-13-43 AT 2400°, 2600°, AND 2800° F

Coating (1)	Specimen	Time for failure[2] (hr) at -		
		2400° F	2600° F	2800° F
M-37-13	1	7	4	1
	2	4	$7\frac{1}{2}$	$1\frac{1}{2}$
M-37-13-43	1	4	$7\frac{1}{2}$	$7\frac{1}{2}$
	2	5	4	5

[1]M-37 designates base coat; succeeding numbers identify seal coats.
[2]As indicated by visible fumes of molybdenum trioxide.

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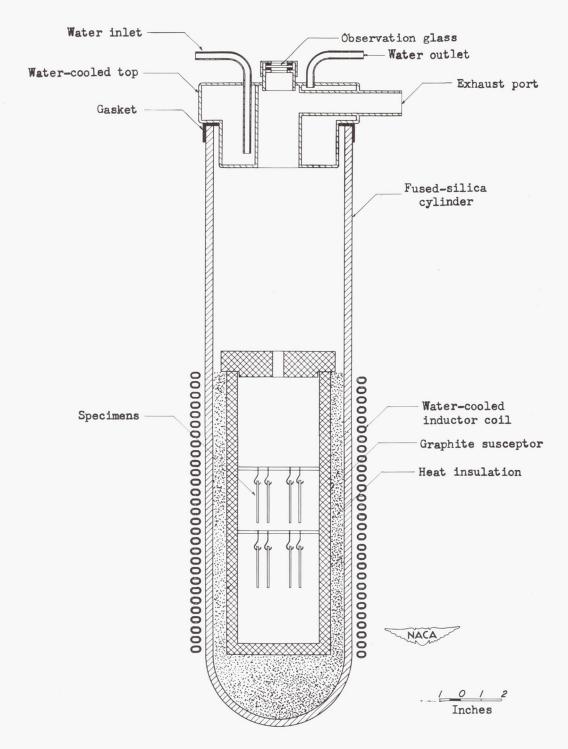
Figure 1.- Schematic drawing of induction furnace used when chromium-
type coatings were fired on molybdenum in graphite susceptor using
partial vacuum or argon atmosphere. Temperature, which was measured
with an optical pyrometer, was controlled by manual adjustment of the
power source which consisted of a 25-kilowatt, 25,000-cycle-per-second,
mercury-arc converter.
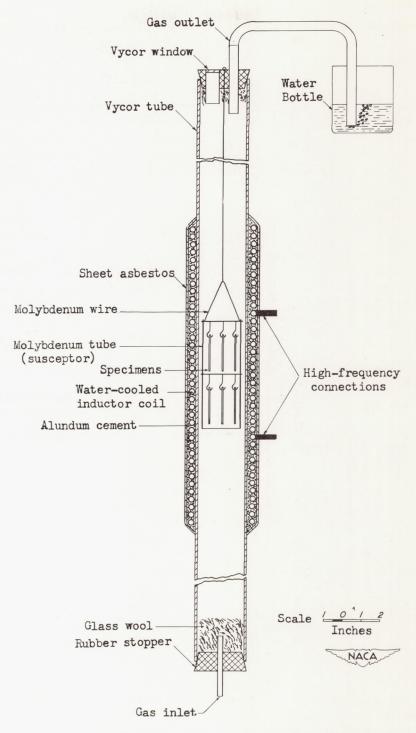
Figure 2.- Schematic drawing of induction furnace used when chromium-type coatings were fired on molybdenum in either tank argon or purified hydrogen. Temperature during firing measured with optical pyrometer. Power source consisted of 25-kilowatt, 25,000-cycle-per-second, mercury-arc converter.

Fixed support

Gastight
porcelain tube

0.080" diam. molybdenum
wire specimen (coated
except for $1\frac{1}{2}"$ at
each end)

Control
couple

$\frac{1}{2}"$ gage length (small
platinum wires cemented
to specimen $\frac{1}{2}"$ apart)

Nichrome coil-type
winding

Ends left open
during test

0   1   2   3

Inches

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Weights
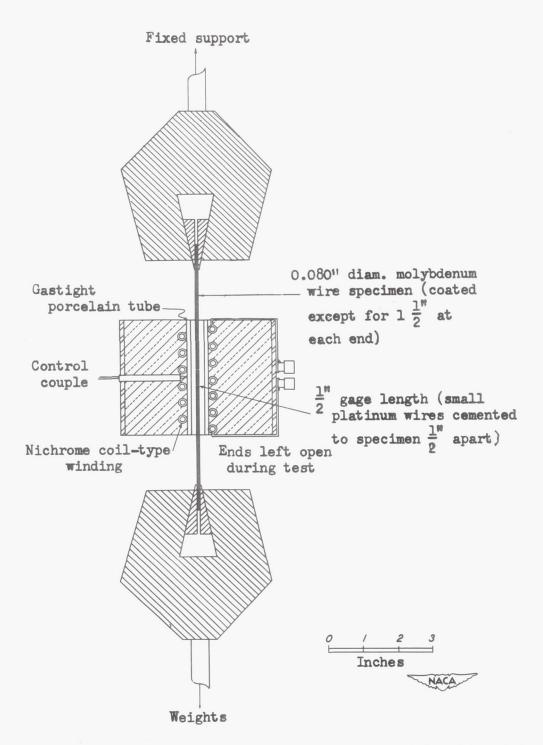
Figure 3.- Schematic drawing showing arrangement used for determining
creep rate of coated molybdenum specimens in temperature range of
1500° to 1800° F. Elongation over gage length of specimen measured
at room temperature after various intervals at constant load and
constant temperature.
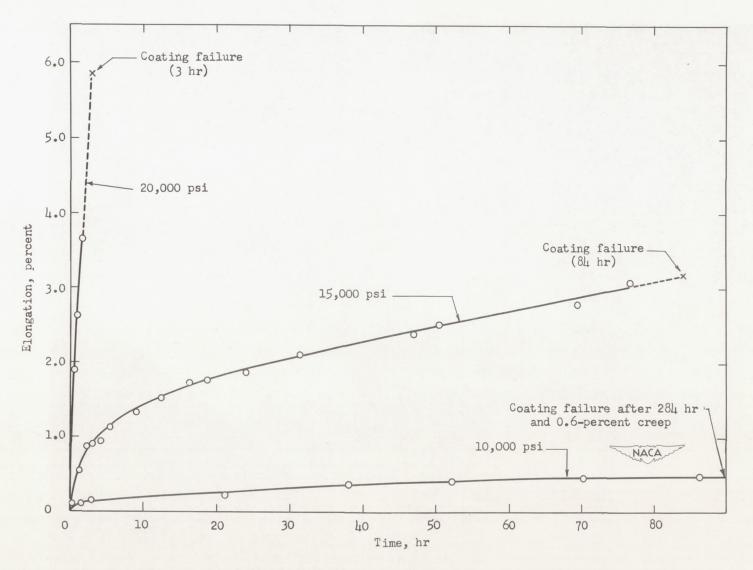
Figure 4.- Percentage-elongation and time curves for three molybdenum
specimens coated with M-39-13 and tested at 1650° F.
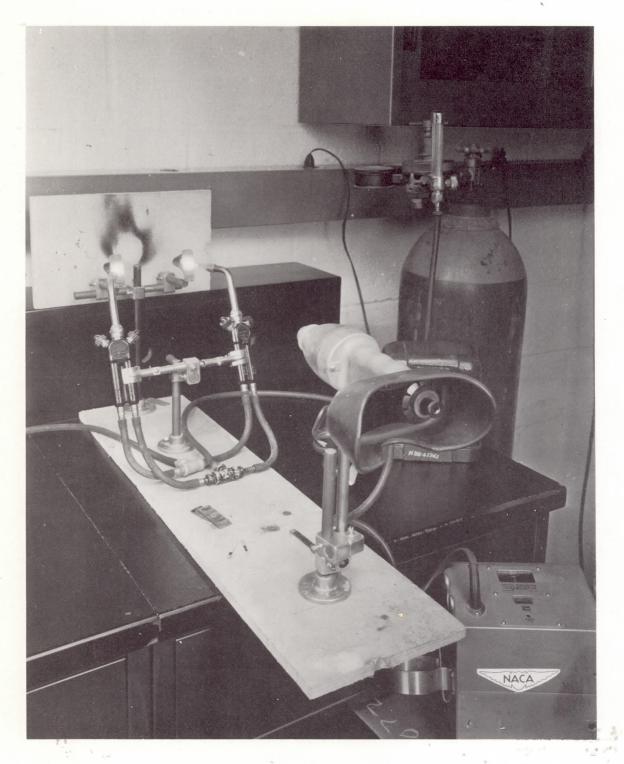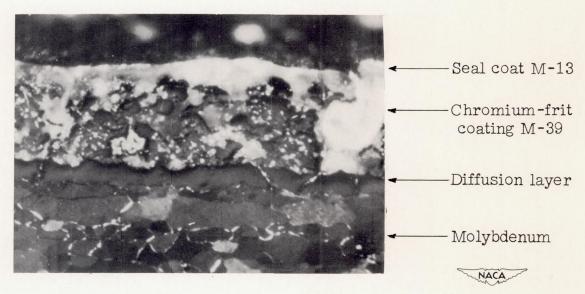
Figure 5.- Arrangement used for flame testing of coated molybdenum
specimens.

(a) Normal vertical illumination.

(b) Same field as shown in (a) taken
with polarized light.

Figure 6.- Photomicrographs (X150) taken to show presence of seal
coat M-13 on chromium-frit coating M-39. Specimen had been
subjected to thermal shock for 25 cycles from 1800° F prior to
sectioning. Cracks in coating appear in (b) to have been sealed
by the glassy phase. Cavities in coatings of type shown at right
in this section were uncommon. Etched in nitric acid.
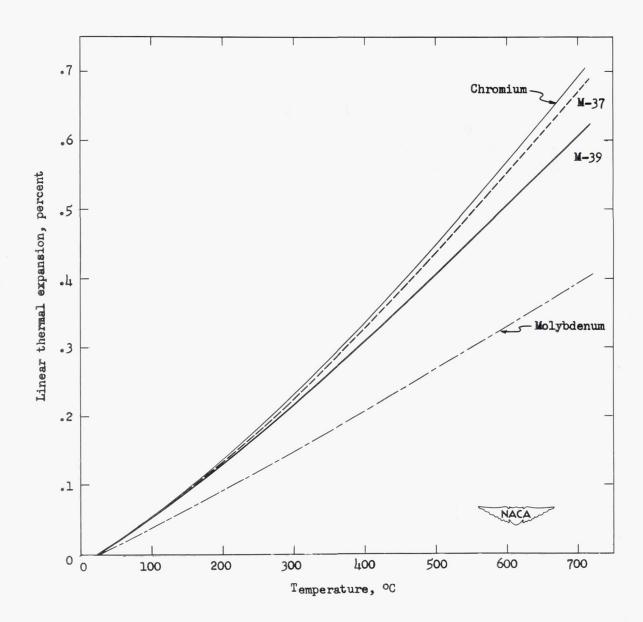
Figure 7.- Linear thermal expansion curves for chromium-frit coating
materials M-37 and M-39 in comparison with reported expansion of
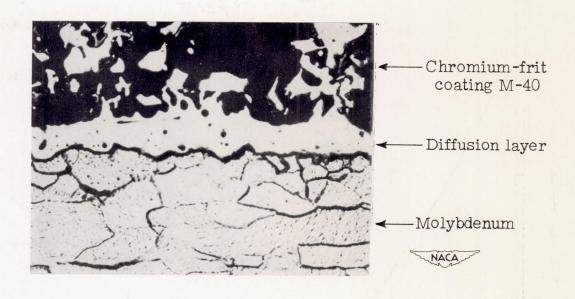chromium (reference 6) and molybdenum (reference 7).

Figure 8.- Photomicrograph (X350) of section through coating-metal
   interface showing presence of diffusion layer that forms when
   chromium-frit-type coatings were applied to molybdenum. Note
   adhesion of chromium particles to diffusion layer and to each
   other. Glass phase (frit 331) is dispersed throughout chromium
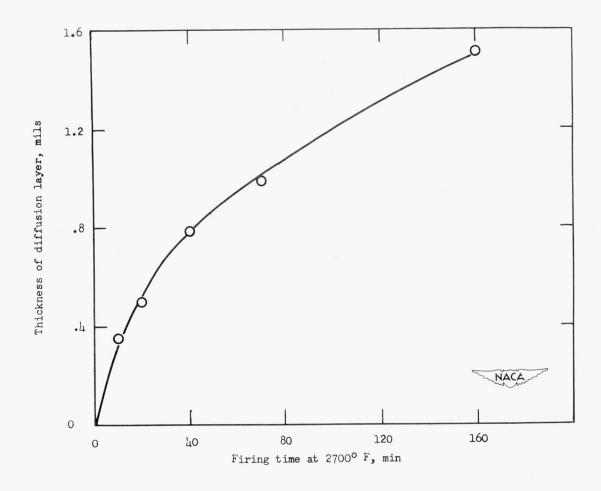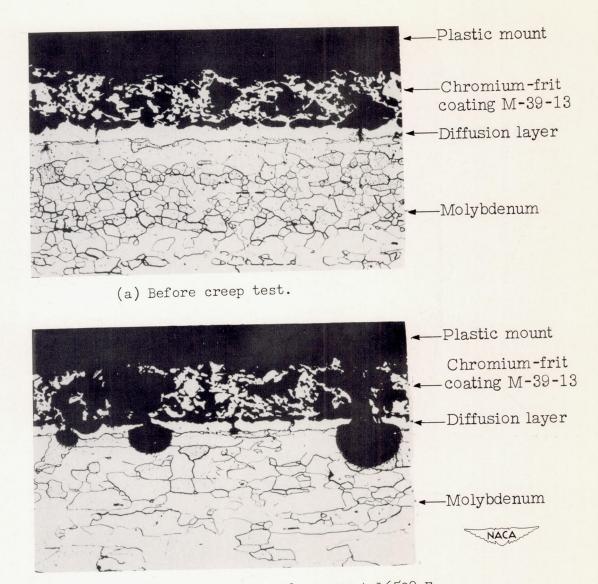   network. Etched in 50 percent nitric acid.

Figure 9.- Effect of firing time at 2700° F in dry hydrogen on thickness of chromized layer for molybdenum specimen coated with M-39. Chromized layer forms at molybdenum surface by diffusion of chromium from coating.

37

— Plastic mount

— Chromium-frit
coating M-39-13

— Diffusion layer

— Molybdenum

(a) Before creep test.

— Plastic mount

Chromium-frit
— coating M-39-13

— Diffusion layer

— Molybdenum

(b) After 3.3-percent creep in 178 hours at 1650° F
with a load of 15,000 psi.

Figure 10.- Photomicrographs (X150) showing type of coating failure
encountered when 0.080-inch-diameter molybdenum wires are coated
with chromium-frit coating M-39-13 and subjected to long-time
heating under load. Cracks in coating may be caused by either
creep or thermal shock. Oxidation pockets in (b) are caused by
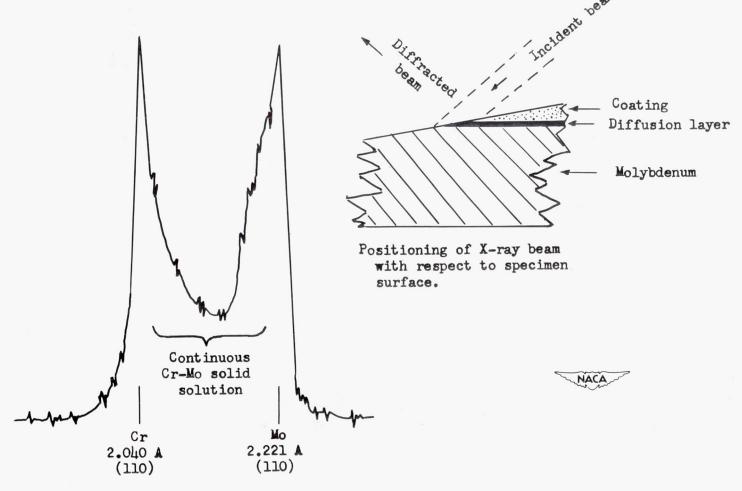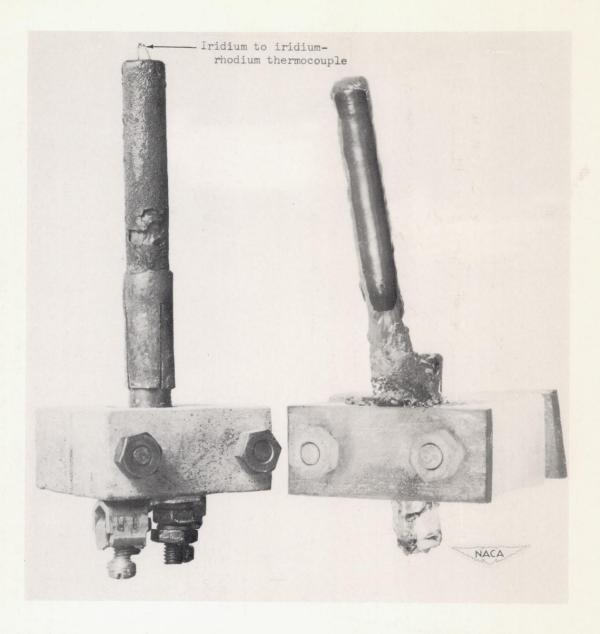slow oxidation of metal through coating crack. Etched in nitric
acid.

Figure 11.- Portion of X-ray diffraction pattern obtained from incident
beam overlapping molybdenum base, chromium-frit coating, and
intervening diffusion layer. Existence of a substantial departure
from base line between two peaks for chromium and molybdenum, coupled
with absence of any well-defined peaks between these limits, indicates
that layer consists of a continuous solid solution.

Iridium to iridium-
rhodium thermocouple

(a) Tube 4 coated with M-38-13 after   (b) Tube 1 coated with M-13 after
    testing for 26 minutes at 1950° F,   testing for 2 minutes below
    22 minutes at 2300° to 2600° F, and   2900° F and 3 minutes at 2900°
    20 minutes at 2900° to 3000° F.   to 3000° F.

Figure 12.- Two coated molybdenum protection tubes after test treatments
    in combustion chamber operated under highly oxidizing conditions. At
    maximum indicated temperature conditions, gas velocity was 1560 feet
    per second, pressure was 14 inches of mercury (gage), and fuel-air
    ratio was 0.040. One of the three M-38-13 tubes tested withstood
    92 minutes at this maximum condition before failure occurred. Complete
    burn-through is shown on leading edge of tube coated with M-13.